

Physical Morphology and Quantitative Characterization of Chemical Changes of Weathered PVC/Pine Composites

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Abstract This study investigated weathering effects on polyvinyl chloride (PVC) based wood plastic composites (WPC), with a focus on the color and structure that is attributed to the material composition. It is directed towards quantifying the main chemical modifications, such as carbonyl and vinyl groups which are formed during weathering. These composites were subjected to three weathering regimes: exterior, accelerated xenon-arc, and accelerated UVA. The change in color was monitored using colorimetry. Fourier transform infrared spectroscopy was used to identify and quantify the chemical modifications (carbonyl formation and vinyl propagation) due to weathering. Additionally, scanning electron microscopy was employed to observe the physical morphological changes that occurred. The results showed that exterior and accelerated xenon-arc and UVA weathering regimes increased the degree of lightness, total color change, carbonyl concentration, and wood loss on the surfaces of the weathered composites. The increased carbonyl concentration during weathering implied that degradation had occurred by oxidation process. Also, oxidation and lignin (from the wood) degradation influenced the color (lightness) of PVC based WPC upon weathering.

Keywords Color change · Carbonyl concentration · Weathering · Wood plastic composites

Introduction

Polyvinyl chloride (PVC) is the most commonly used amorphous plastic and has some admirable characteristics such as light-weight, durable, waterproof, and biologically, flame and chemically resistant [1–3]. In its rigid form, PVC is weather-resistant when extruded into house siding, pipes, and gutters [1]. Incorporation of impact modifiers and stabilizers make it a popular material for window and door frames. As a building material, PVC is inexpensive and easy to install.

The PVC world market grew with an average rate of approximately 5% in the previous years and its supply is anticipated to reach a volume of 40 million tons by the year 2016 [4]. The wood plastic composite (WPC) industry accounted for about 7% of the world PVC consumption in 2003 and consumed even higher i.e. 10–13% in 2004 [5, 6]. PVC based WPCs are gaining entry into the construction and building industries because of its thermal stability, moisture resistance, and stiffness [4, 7]. Additionally, PVC based WPCs are superior to high density polyethylene (HDPE) and polypropylene (PP) based WPC with respect to their higher modulus, good creep resistance, weatherability, and flame retardance [8–11]. Despite the increasing demand for WPC by consumers, growth in its exterior applications has raised concerns about its long-term weatherability and durability. It is generally known that in the natural environment, UV radiation from sunlight, temperature, moisture, humidity, bacteria, and molds are the factors that induce photodegradation and biodegradation progression of PVC [2, 12]. Theoretically, PVC is not expected to absorb light of wavelength longer than 190–220 nm because an ideal PVC macromolecule contains only C–C, C–H, and C–Cl bonds [12]. In reality, studies have established the susceptibility of PVC substances to incident light of

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300–400 nm wavelengths [13]. This is because commercially available PVC contains minor amounts of defects, such as random unsaturation (allylic chlorine), chain end groups, and branch points (tertiary bonded chloride atoms and oxidized structures) [12]. Unfortunately, incorporation of wood, whose polymers are susceptible to the absorption of wavelength of 300–400 nm, makes PVC based WPC more photo-labile. It was observed that incorporation of wood fibers into the PVC matrix promotes and/or accelerates photodegradation of the polymeric matrix [14]. Also, the pronounced discoloration of the PVC/wood composites was attributed to the addition of the carbonyl functional groups of the wood fibers within the polymer matrix during manufacturing [14].

Matuana et al. [15] acknowledged that it is generally accepted that the photodegradation of PVC results in rapid color change because of the formation of alkene or polyene linkages. The fact is, dehydrochlorination leads to the formation of long, conjugated polyene sequence $(-\text{CH}=\text{CH}-)_n$ in the polymer chains, which give the red-brown color of degraded product [16]. The photo-elimination process that occurs during weathering creates Cl (chlorine) radicals that are able to initiate oxidation chains in the presence of atmospheric oxygen. This oxidation leads mainly to β -chlorocarboxylic acids, ester or α - α' -dichloroketones, and γ -peracids or acid chlorides [17]. In addition to HCl elimination, other volatile products that are formed include water and carbon monoxide [17].

Additionally, chain scission and cross-linking, which also occur due to the elimination step cause deleterious effects on the mechanical properties [15]. Other associated problems of outdoor exposure of PVC based WPC include whitening, loss of gloss or yellowing [18]. These ageing effects of WPC are mainly due to oxidation and photo-oxidation which occur during the initial processing stage and during their service lifetime, respectively [15].

Market analysis has shown that consumers prefer building materials that are durable and require low routine maintenance [19]. Consequently, manufacturers have to produce WPC with improved weathering performance. Therefore, initial screening of composites for their weatherability is very important. To assess the weatherability of WPC materials, colorimetry and Fourier transform infrared (FTIR) spectroscopy have been frequently employed to monitor color and chemical changes, respectively. Quantitative determination as to the extent of oxidation, as carbonyl groups, at weathered WPC surfaces has been successfully determined by FTIR spectroscopy [20]. Application of this quantitative approach to carbonyl groups present in PVC based WPC will aid in understanding the mechanism of weathering.

The outcome of weathering studies under natural conditions and accelerated tests depends on several factors

such as range of the light spectrum radiation, temperature, moisture, and some external agents. Introduction of accelerated weathering testers enhances weathering study within a minimum possible time. Among various accelerated weathering testers, xenon arc and UVA 340 are the most commonly used [21]. Unfortunately, there is no correlation between xenon arc and UVA 340; but xenon arc source gives the best correlation with daylight exposures [22]. Xenon arc light sources reproduces the entire spectrum of sunlight such as ultraviolet (UV), visible light, and infrared (IR) but UVA 340 does not. UVA 340 concentrates more on the lower wavelength spectrum (300–400 nm) that causes damaging effects on polymers. In xenon arc weathering systems, moderately cold water is sprayed onto a relatively hot test specimen; thereby causing thermal shock. Furthermore, xenon arc weathering systems is recommended for investigating color change.

The purpose of this study is to investigate how PVC based WPCs weather under natural and accelerated (xenon-arc and UVA) weathering regimes. The surface weathering of the WPCs were monitored by a combination of colorimetry, FTIR spectroscopy and scanning electron microscopy.

Materials and Methods

A commercial rigid PVC compound (LP, Geon E4000 Natural 0000) and pine wood fiber (60-mesh, supplied by American Wood Fibers) were used for the production of wood plastic composites (WPC). The PVC-based WPC studied consist of 50:50 of PVC and wood (on weight basis). The dry premixed formulation was extruded on a 35 mm conical counter rotating twin-screw extruder (Cincinnati-Milacron) to a profiled dimension of 9.5 mm \times 38 mm. The extruded profiles were then knife milled to a thickness of 5 mm for the weathering tests because many commercial WPC products are surface finished.

WPC Weathering

Natural weathering test was conducted by exposing the WPC specimens (5 mm \times 38 mm \times 610 mm) outside in Moscow, Idaho, USA on a south-facing wall at an angle of 45° in accordance with ASTM D 1435 [23]. These specimens were exposed exterior for a total period of 2-year and sampled periodically. Another set of specimens (5 mm \times 38 mm \times 101 mm) were subjected to accelerated weathering tests in UVA (UV2000, Atlas) and xenon-arc (Q-Sun Panel) weatherometers. They were subjected to an accelerated weathering procedure (average irradiance = 0.70 W/m² at 340 nm, chamber temperature = 70 °C, and water spray) following ASTM D 6662 [24], which is the only standard for monitoring composites' surface

appearance changes. Specimens were periodically withdrawn for color and chemical characterization between 0 and 2000 h exposure time. The samples collected from PVC/pine composite before weathering (0 h) would henceforth be referred to as unweathered WPC while those collected after subsequent exposure for a given time would be referred to as weathered WPC.

Data Collection

Physical Morphology Characterization

Sections of unweathered and weathered (400- and 2000-h xenon-arc-weathered as well as 2-year exterior-weathered) WPC were cut into approximately 8 mm × 8 mm specimens leaving the exposed surface for analysis. The samples were mounted using carbon tape and examined on a LEO Gemini field emission scanning electron microscope (SEM). The specimens were analyzed directly (without coating) at 1 kV.

The color change that occurred during the weathering of WPC surface was monitored using a StellarNet EPP2000 UV–Vis spectrometer (190–850 nm), krypton light source (SL1, StellarNet), with a diffuse reflection fiber optic probe in accordance with ASTM D 2244 [25]. The spectrometer's SpectraWiz software transforms spectral data into CIELAB color coordinates (L^* , a^* and b^*) based on a D65 light source [26]. Five replicates per WPC sample were measured at three locations on each specimen. The total difference in color (ΔE_{ab}) was computed as described in a previous study [20].

Chemical Characterization

Infrared Spectroscopy Analysis

Infrared spectroscopy was employed to examine the chemical (functional groups: carbonyl, vinyl, and hydroxyl) changes during the weathering of the composites. Spectra were collected using a ThermoNicolet Avatar 370 FT-IR spectrometer operating in the attenuated total reflection (ATR) mode (SmartPerformer, ZnSe crystal). The procedures involved during spectra acquisition and data computation are fully described by Fabiyi et al. [20]. Additionally, the concentrations of the carbonyl groups were computed following the protocol developed by Fabiyi et al. [20], which is based on Beer–Lambert equation with some assumptions [27–30] as:

$$c = A / (2d_p \cdot \epsilon) \quad (1)$$

where c is the molar concentration of the functional group mol/L (M), A is the absorbance of the functional group band in the infrared spectrum, ϵ is the molar absorptivity

(L/mol/cm), and d_p is the ATR depth of penetration. The values of molar absorptivities for model carboxylic acids (1718 cm^{-1}), esters (1744 cm^{-1}), γ -peracids (1777 cm^{-1}), and vinyl groups (1635 cm^{-1}), which are 350, 590, 720, and 121 L/mol/cm, respectively were used [31]. Molar absorptivities values used are based on polyethylene, and can be applied to PVC based materials since both plastics have similar carbon backbone (Dr. Peter Griffiths, personal communication).

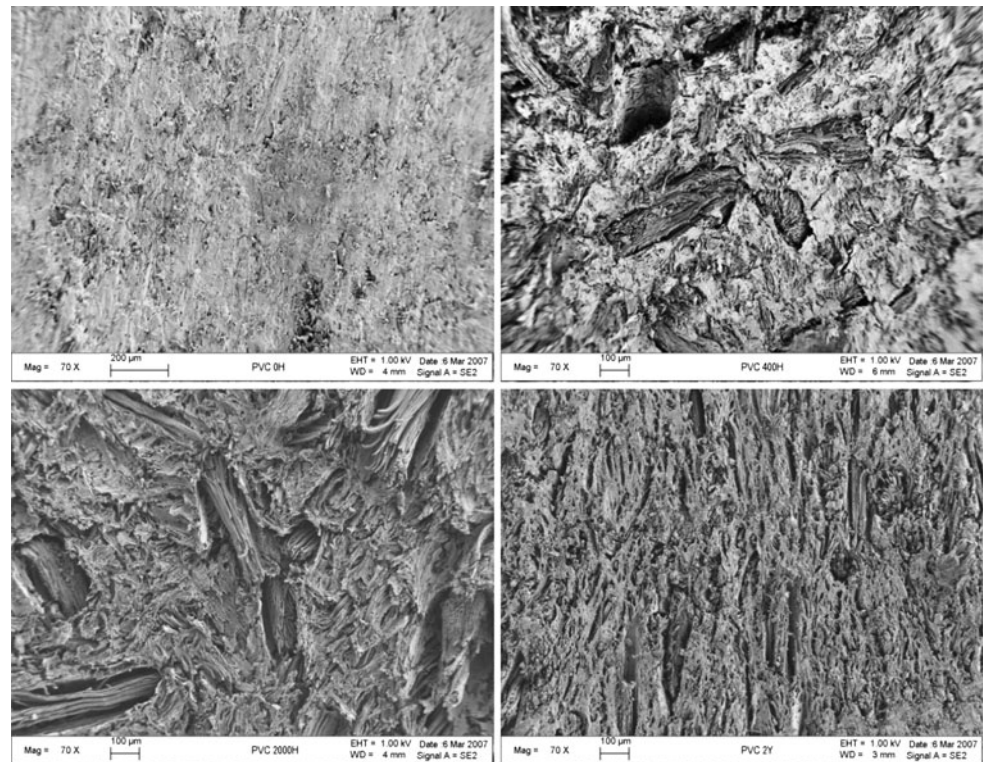
In order to determine the effect of weathering on wood polymers (lignin, cellulose, and hemicelluloses), a conventional approach was employed by calculating the lignin and hydroxyl indices of the weathered products. Lignin index (LI) was taken as the ratio of the area (absorbance) of the band at $1512\text{--}1508 \text{ cm}^{-1}$ and the antisymmetric C–H stretching band of methylene groups ($2917\text{--}1912 \text{ cm}^{-1}$). Additionally, hydroxyl index (HI) was taken as the ratio of the area (absorbance) of the band at $3500\text{--}3080 \text{ cm}^{-1}$ and the antisymmetric C–H stretching band of methylene groups ($2917\text{--}1912 \text{ cm}^{-1}$). The latter band was chosen as a reference because it changed minimally during weathering [20].

Results and Discussion

Visual Appearance and Surface Cracking

Visual assessment revealed that xenon-arc accelerated and UVA accelerated weathered WPC yellowed at initial exposure stage. The exterior weathered WPC samples lightened initially (first 8 months), then darkened as mildew or mold and dirt were adhered on the surface. The practical significance of this is that natural weathering factors are more complex than a controlled or laboratory accelerated weathering test. Figure 1 shows SEM micrographs of unweathered, 400, and 2000 h xenon-arc accelerated weathered and 2-year exterior weathered WPC. PVC and wood erosion was observed at the surface by SEM on the weathered PVC composites (Fig. 1). This may be caused by the depolymerization of the wood particles and PVC thereby resulting in pitted surface. In addition, erosion of wood particle leaves crevices around the plastic matrix or in some cases the wood particles are absent. Surface pits and erosion occurred around 400 h and qualitatively their frequency and size increased upon extended weathering. These findings are in agreement with the literature [20, 32]. This effect may be due to water sorption (during water spraying) and desorption (during isothermal (70°C) conditioning period with no water spray), thereby causing cracks between wood and plastic interface which is enhanced by subsequent erosion. From the SEM analysis, a sequential degradation occurred: (1) the surface layer was

Fig. 1 Scanning electron micrographs (70 \times) (*top-left*) unweathered control, (*top-right*) 400 h xenon-arc weathered, (*bottom-left*) 2000 h xenon-arc weathered, and (*bottom-right*) 2-year exterior weathered PVC/pine composites



eroded thereby creating crevices on the surface at the early stage of exposure, (2) protracted exposure time during xenon-arc and exterior weathering caused increase in the frequency and size of the cavities, and (3) further prolonged exposure resulted in the development of small cracks on the weathered surface. It is suggested therefore that a combination of plastic and wood degraded at the WPC surface after a very protracted weathering period.

Color Changes of Weathered WPC

Figures 2 and 3 shows the changes in lightness (ΔL) and total color (ΔE_{ab}) at different exposure times of the WPCs subjected to natural and accelerated weathering regimes. For PVC-based WPC, ΔL and ΔE_{ab} increased upon weathering until 1200 h for the xenon-arc weathered composites (Fig. 2). ΔL and ΔE_{ab} observed for weathered composites differed between xenon-arc and UVA. Xenon-arc caused a significant increased in lightness and total color change while UVA did not. During xenon-arc weathering, the ΔE_{ab} increased to nearly 41 at 1200 h for PVC composites. However, a lower ΔE_{ab} value = 14 was observed for UVA weathered at the same exposure time. The results are consistent with a previous study [15]. The major drop in ΔE_{ab} at 1200 h and 1600 h for WPC subjected to xenon arc and UVA weathering systems, respectively may be due to the contribution of other color coordinates. From Fig. 2, it is clear that the degree of

lightness (or darkening) follow the same trend with ΔE_{ab} . More importantly, previous report showed that color change in wood during weathering was due to the lignin degradation [33]. Infrared spectra show a significant decrease in lignin content due to prolonged weathering (Fig. 4). Therefore, the drop in ΔE_{ab} may be because of the fact that the quantity of lignin remaining on the weathered WPC could no longer sustain the formation of more chromophores which are responsible for color change. The depletion instead of formation of these chromophores because of protracted weathering may lead to the drop in ΔE_{ab} . The lightness (ΔL) increased significantly throughout the exterior exposure period. However, the total color change (ΔE_{ab}) increased up to the seventh month (210 days) of exterior exposure. Thereafter, the ΔE_{ab} decreased drastically at the end of the 8 months with an insignificant change throughout the remaining 16 months of exposure. Infestation of the exterior weathered composites with molds and/or mildew might have also contributed to the drop in ΔE_{ab} .

Surface Chemistry by Infrared Spectroscopy

The infrared spectra of unweathered and weathered composites show that some functional group changes (bands) had occurred upon exposure (Fig. 4). For instance, the spectral structures between 1015 and 1050 cm^{-1} region which was assigned to C–O groups in wood (holocellulose)

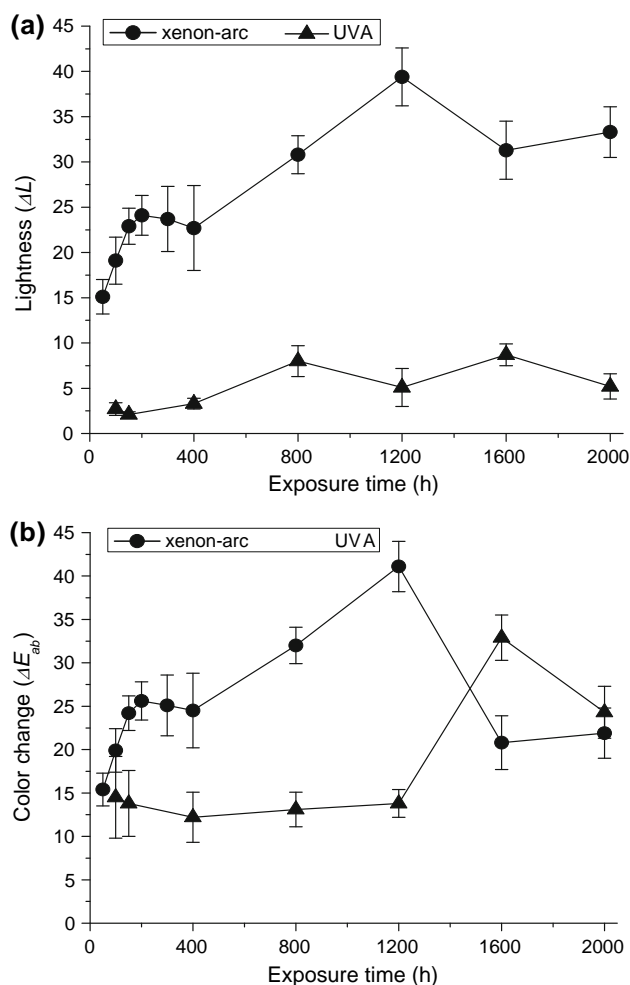


Fig. 2 Effect of xenon-arc and UVA accelerated weathering on the **a** lightness (ΔL) and **b** total color change (ΔE_{ab}) of PVC/pine composites (mean for each, $n = 5$ with error bars equal to ± 1 standard deviation)

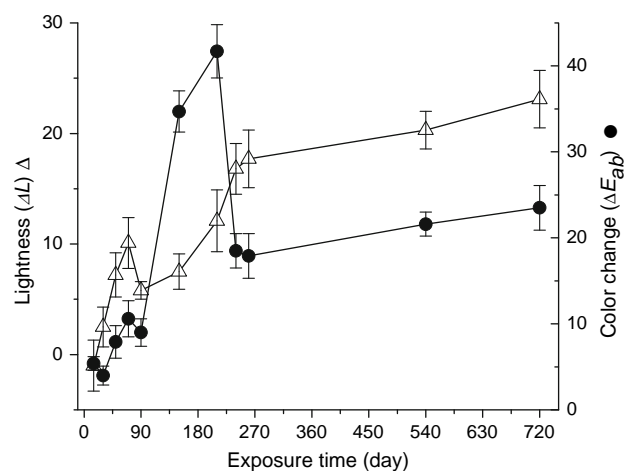


Fig. 3 Effect of exterior weathering on the lightness (ΔL) and total color change (ΔE_{ab}) of PVC/pine composites (mean for each, $n = 5$ with error bars equal to ± 1 standard deviation)

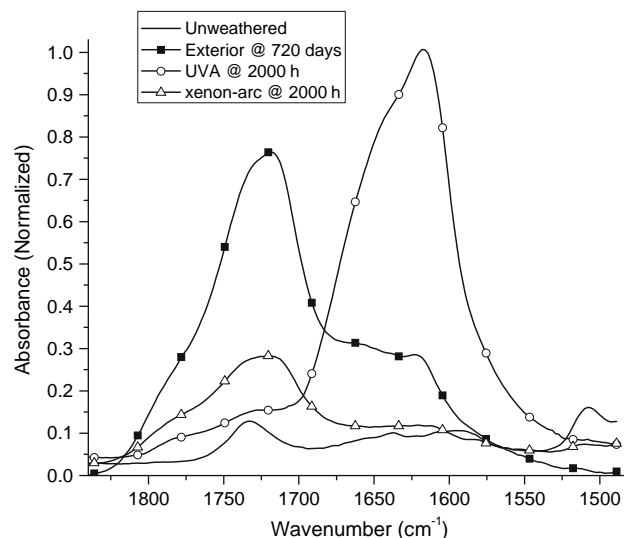


Fig. 4 IR spectra showing the vinyl and carbonyl region of unweathered, exterior, UVA, and xenon-arc weathered PVC/pine composites

decreased upon extended weathering time [34, 35]. Additionally, the intensity of the lignin ether linkage assigned band ($1508\text{--}1512\text{ cm}^{-1}$) decreased with longer exposure time; which is in agreement with previous studies [15, 20].

The band between 1650 and 1630 cm^{-1} , which is assigned to the polyene (vinyl) group, increased in concentration from 8.3 mol/kg (0 h) to 16.1 mol/kg (1200 h) in xenon arc weathered composites. However, a significant increase in polyene concentration occurred in the UVA weathering system from 8.3 mol/kg at 0 h to 39.6 mol/kg at 2000 h . This indicates the incidence of HCl elimination in the PVC thereby resulting into double bonds formation; suggesting the degradation of PVC during weathering at the UV region. This is an indication that PVC also degrades during weathering. Additionally, the band between 1680 and 1800 cm^{-1} is assigned to carbonyl groups (Fig. 4). Oxidation of the composites' surface is significantly high as the carbonyl groups increased drastically. Carbonyl groups increased significantly for weathered PVC composites compared to studies on HDPE- and PP-based WPC subjected to similar weathering conditions [20]. It is important to note that two new carbonyl groups appeared in the IR spectra at 1722 and 1772 cm^{-1} due to weathering effect as shown in Fig. 4. The absorption band at 1722 cm^{-1} is a β -chlorocarboxylic acid [36], while the band at 1772 cm^{-1} is assigned to γ -peracid (or acid chloride) [17]. The carbonyl groups that are present upon weathering include: (1) β -chlorocarboxylic acids ($1725\text{--}1715\text{ cm}^{-1}$), (2) esters (or α - α' -dichloroketones) ($1745\text{--}1730\text{ cm}^{-1}$), and (3) γ -peracids ($1800\text{--}1765\text{ cm}^{-1}$) [17] (Fig. 4).

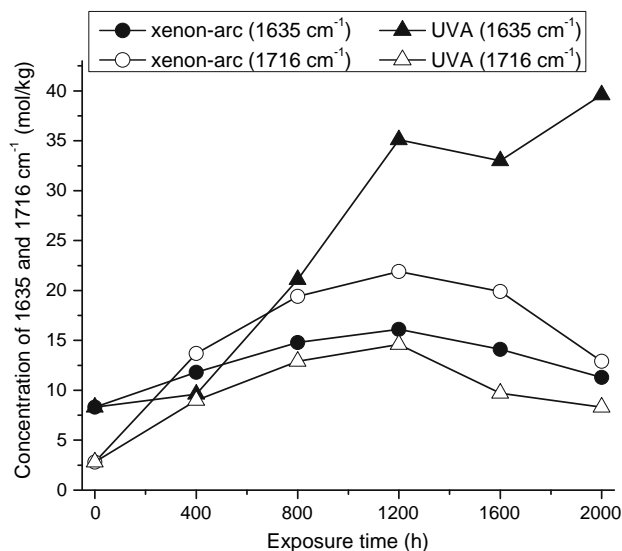


Fig. 5 Effect of xenon-arc and UVA accelerated weathering on vinyl (1635 cm^{-1}) and β -chlorocarboxylic acid (1716 cm^{-1}) concentration of PVC/pine composites

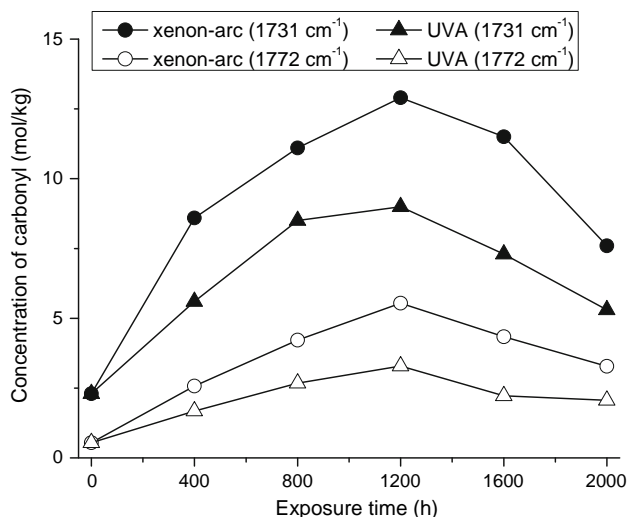


Fig. 6 Effect of xenon-arc and UVA accelerated weathering on esters (1731 cm^{-1}) and γ -peracids (1772 cm^{-1}) concentration of PVC/pine composites

The effect of exposure time on the concentrations of β -chlorocarboxylic acids, esters, and vinyl groups are shown in Figs. 5, 6 and 7. At the early stage of xenon-arc and UVA weathering (up to 1200 h), the concentrations of the carbonyl and vinyl groups increased. However, protracted weathering caused these concentrations to decrease. For the exterior weathered composites, both the carbonyl and vinyl concentrations continued to increase throughout the 2-year exposure period. The relationships between carbonyl concentrations and color changes (ΔL and ΔE_{ab})

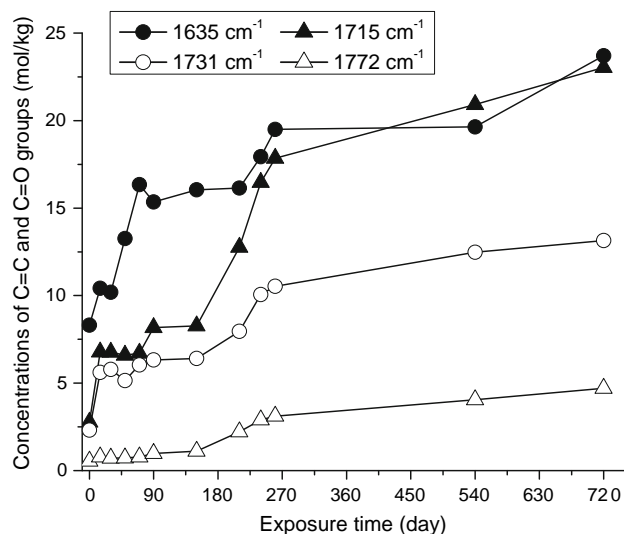


Fig. 7 Effect of exterior weathering on vinyl (1635 cm^{-1}), β -chlorocarboxylic acid (1715 cm^{-1}), esters (1731 cm^{-1}), and γ -peracids (1772 cm^{-1}) concentration of PVC/pine composites

of PVC-based WPC for different weathering regimes are given in the following equations (Eqs. 2–6):

$$\Delta L(\text{xenon-arc}) = 1.107 * C_{\text{total}} - 5.996, \quad R^2 = 0.995 \quad (2)$$

$$\Delta E_{ab}(\text{xenon-arc}) = 1.152 * C_{\text{total}} - 5.994, \quad R^2 = 0.99 \quad (3)$$

$$\Delta L(\text{UVA}) = 0.312 * C_{\text{total}} - 1.582, \quad R^2 = 0.78 \quad (4)$$

$$\Delta E_{ab}(\text{UVA}) = 0.636 * C_{\text{total}} - 1.814, \quad R^2 = 0.85 \quad (5)$$

$$\Delta L(\text{exterior}) = 0.730 * C_{\text{total}} - 2.793, \quad R^2 = 0.89 \quad (6)$$

where, (1) C_{total} is the summation of the concentrations of β -chlorocarboxylic acids, (2) esters, and (3) γ -peracids.

These models imply that there was a strong relationship between total color change (ΔE_{ab}) and total carbonyl concentration as well as lightness (ΔL) and total carbonyl concentration of xenon-arc and UVA weathered PVC based WPC. However, this relationship only holds for the lightness (ΔL) and total carbonyl concentration of exterior weathered PVC based WPC. Therefore, oxidation leads to an increased lightness and total color change of weathered PVC-based WPC. Note that the data obtained for 1600 and 2000 h were not included in the development of Eqs. 2–5, where evidence of lack of relationship occurred. However, the entire exterior exposure time (from 0 to 2-year) was employed in the development of Eq. 6. More importantly, developing a relationship for color and chemical changes of the WPC of outdoor weathering in this manner could be misleading. Therefore, this relationship is only valid for weathering exposure in the studied geographical area, during the time frame studied, and for the WPC studied.

The practical implications of this study are: (1) color and concentration of the carbonyl group measurement suggest that there is a strong relationship between the two, (2) the drastic drop in the total color change but continual carbonyl concentrations increase during exterior exposure emphasizes the fact that an infestation by mildew may be responsible for the decrease in color change, and (3) restricting the carbonyl formation during the service life of the composite may likely enhance its color stability.

The degradation of wood component of the WPC was estimated based on the anti-symmetric C–H stretching band of methylene groups. The lignin index decreased with increase in the exposure time for all the weathering regimes (Fig. 8). This indicates that lignin degradation occurs during weathering. Also, the hydroxyl index decreased upon extended exposure time for all the weathering regimes (Fig. 8). The hydroxyl index remained unchanged after 1200 h of WPC weathering in xenon-arc, suggesting

that the levels of cellulose on the surface of weathered WPC is no longer affected after the initial degradation.

Conclusions

The effects of weathering on color and macromolecules of PVC/pine composites were successfully examined and showed that wood degradation and erosion created cracks and “pits” at the surface and increased upon protracted weathering. Additionally, weathering of WPC caused surface lightening and total color change, which continued throughout the exposure time. Furthermore, different weathering regimes had different weathering pattern on the microscopic features and color fade. The increase of polyene functionality and the loss of wood at the weathered WPC surface increased with exposure time. The presence of chlorinated carbonyl groups (β -chlorocarboxylic acids, esters, and γ -peracid) was established by FTIR spectroscopy. The increase in carbonyl concentration provided strong evidence that photodegradation occurred with prolonged exposure time. Additionally, increase in the carbonyl concentrations caused an increase in the color change. The practical significance of this study is that the extent of PVC composite oxidation during weathering can be monitored and modeled based on color change. The derived weathering models could potentially be used to predict the lifespan (color stability) of the composites.

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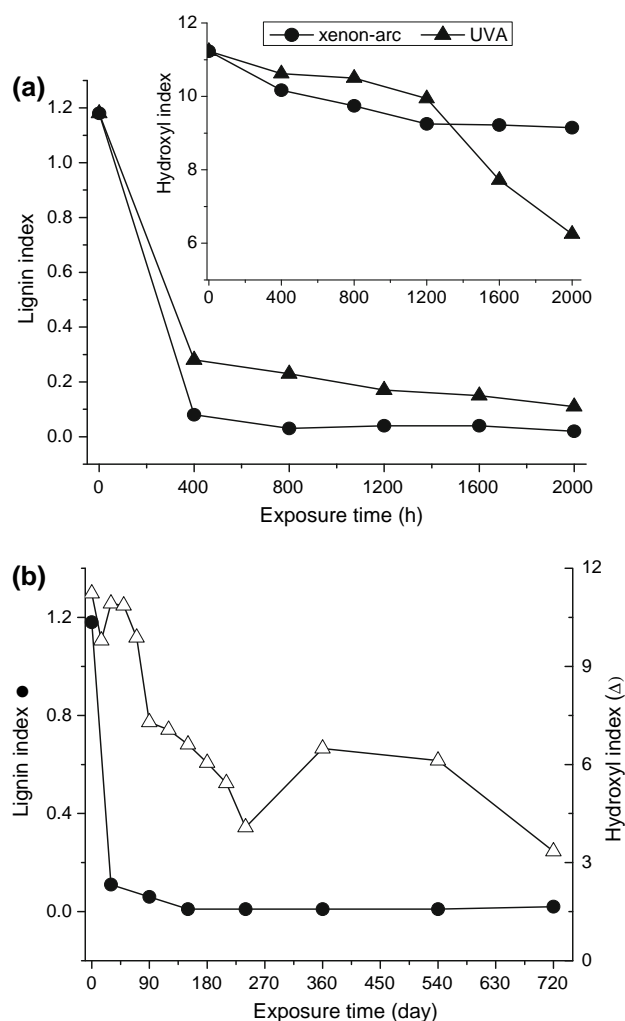


Fig. 8 Effect of **a** xenon-arc and UVA accelerated and **b** exterior weathering on lignin and hydroxyl index of PVC/pine composites

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